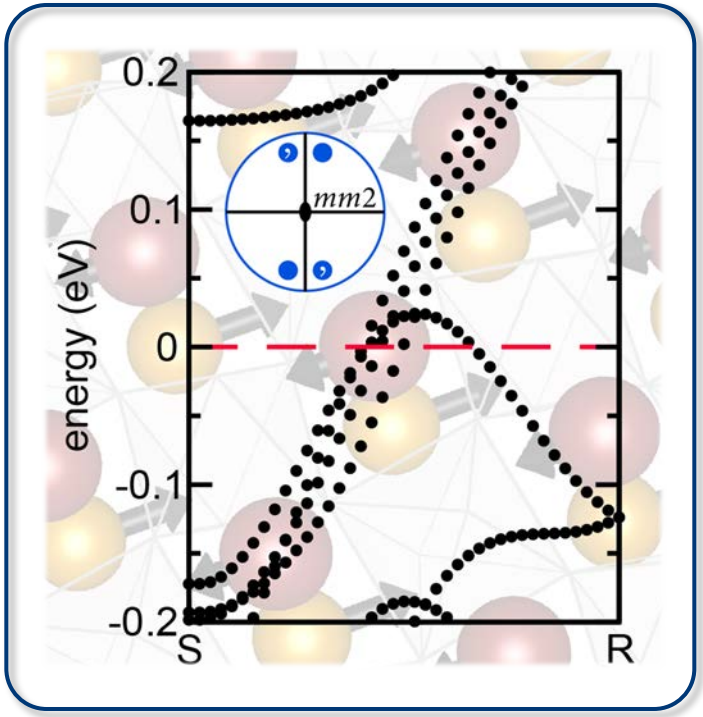
Design of correlated metals without inversion symmetry



James M Rondinelli
Department of Materials Science and Engineering
Drexel University, Philadelphia PA, 19104 USA
email – jrondinelli@coe.drexel.edu

date – May 1, 2014 | Correlated Oxides & Oxide Interfaces

http://mtdg.materials.drexel.edu

materials theory & design group

Drexel UNIVERSITY

Collaborators and Acknowledgments

- Group Members
  - UG – Adam Cordi Paul Cheung
  - GR – Josh Young, Nenian Charles
  - PD – Antonio Cammarata, **Danilo Puggioni**, Prasanna Balachandran

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  - Thin film growth – Steve May (Drexel); Jak Tchakhalian (Arkansas); Darrell Schlom (Cornell); Roman Engel-Hebert (PennState); Anand Bhattacharya (Argonne), **Yuri Suzuki** (Stanford), **Chang-Beom Eom** (Wisconsin)
  - Theory – Craig Fennie (Cornell); Gaoyang Gou (Xi' an Jiaotong Univ.); Nicole Benedek (UT Austin)
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  - Materials characterization – John Freeland, Phil Ryan (Argonne); Albina Borisevich, Sergei Kalinin (Oak Ridge); Venkat Gopalan (PennState)

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ONR Office of Naval Research
DARPA
ACS PRF
XSEDE Extreme Science and Engineering Discovery Environment
Argonne NATIONAL LABORATORY
DOD HPC MODERNIZATION PROGRAM

Summary – Noncentrosymmetric Metal (NCSM) Design

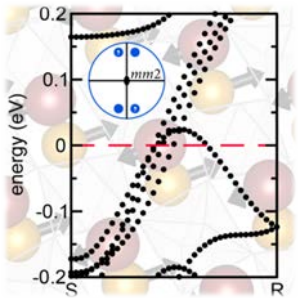
Why are there any NCS metals?

Weak *electron–lattice coupling principle:* The existence of NCSM relies on weak coupling between the electrons at the Fermi level and the *ir-active* phonons responsible for removing inversion

NCS metallic oxides by design

Introduced classification scheme

First-principles design of a polar ruthenate $(Sr,Ca)Ru_2O_6$



nature COMMUNICATIONS
DOI: 10.1038/ncomms4432

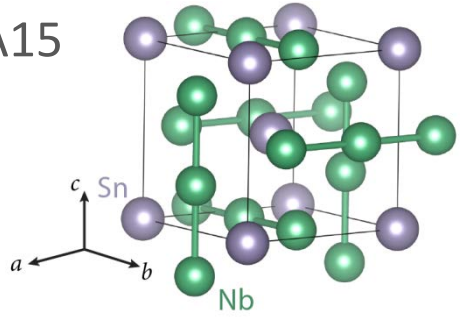
Physical Properties and Applications

- NCS metals may exhibit Seebeck coefficients with large anisotropy
- Ultra-fast heat flux sensors for thermal radiation: measure induced electric current at ends of constant temperature via transverse effects
- Carrier masses are also sensitive to polar distortion

Some history on polar metals

Polar metals and metallic “ferroelectricity”

- Discussed early in the 1960s by Matthias
- Suggestions circulated during early studies of the A15 superconductors (V_3Si and Nb_3Sn)
  - Loss in inversion or appearance of polar axis



VOLUME 14, NUMBER 7 PHYSICAL REVIEW LETTERS 15 FEBRUARY 1965

SYMMETRY CONSIDERATIONS ON MARTENSITIC TRANSFORMATIONS: “FERROELECTRIC” METALS?

P. W. Anderson and E. I. Blount
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 22 December 1964)

- 10 years later V_2Hf identified (Zachariasen, 1972)
- Additional compounds serendipitously discovered thereafter

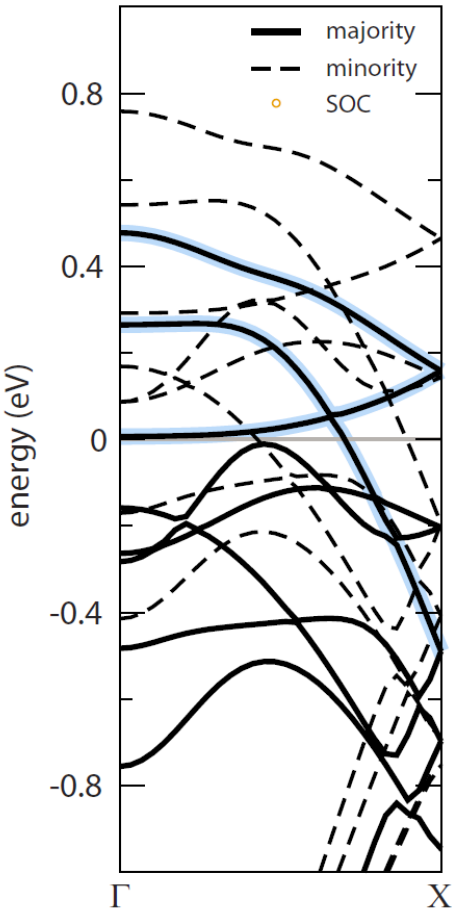
Anderson & Blount, Phys. Rev. Lett., **14**, 217 (1965)

Nomenclature to facilitate the discovery of noncentrosymmetric metals

Operational definition for metallic materials

- Materials with delocalized electrons and one or more free electron-like bands crossing the Fermi level
  - ***Includes*** intrinsic metals or semi-metals with partially occupied (spin-polarized) bands
  - ***Excludes*** degenerately doped ferroelectrics like $BaTiO_3$ or polar oxides Al:ZnO

NB: Do not discount doped ferroelectrics as uninteresting, as they may provide useful understanding within this topic

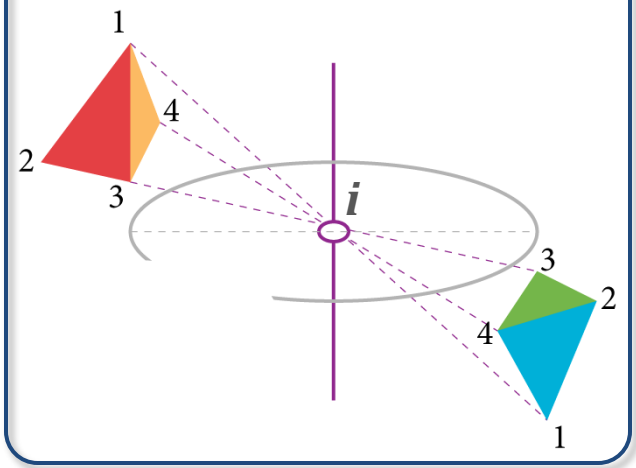


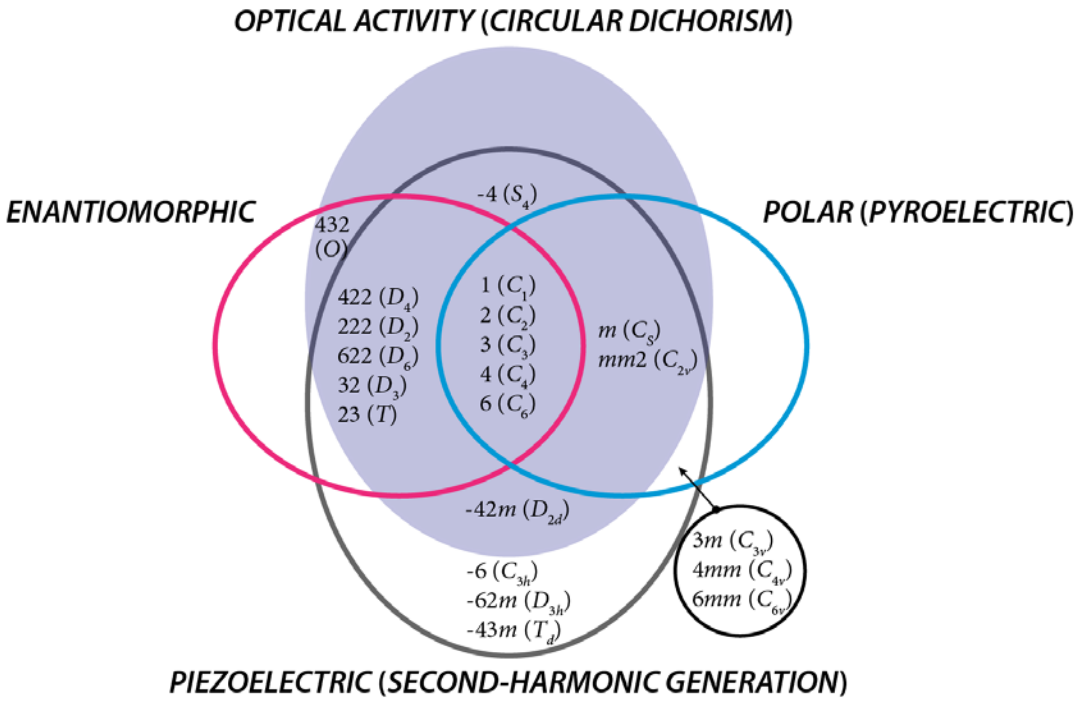
Kolodiazhnyi et al., Phys. Rev. Lett., 104, 147602 (2010); Wang et al., Phys. Rev. Lett., **109**, 247601 (2012)

Crystalline structures without inversion – noncentrosymmetric (NCS) crystal classes

- 21 point groups without inversion, only 11 are polar

Absence of the inversion operation mapping the coordinate (*x*,*y*,*z*) to (*-x*,*-y*,*-z*)

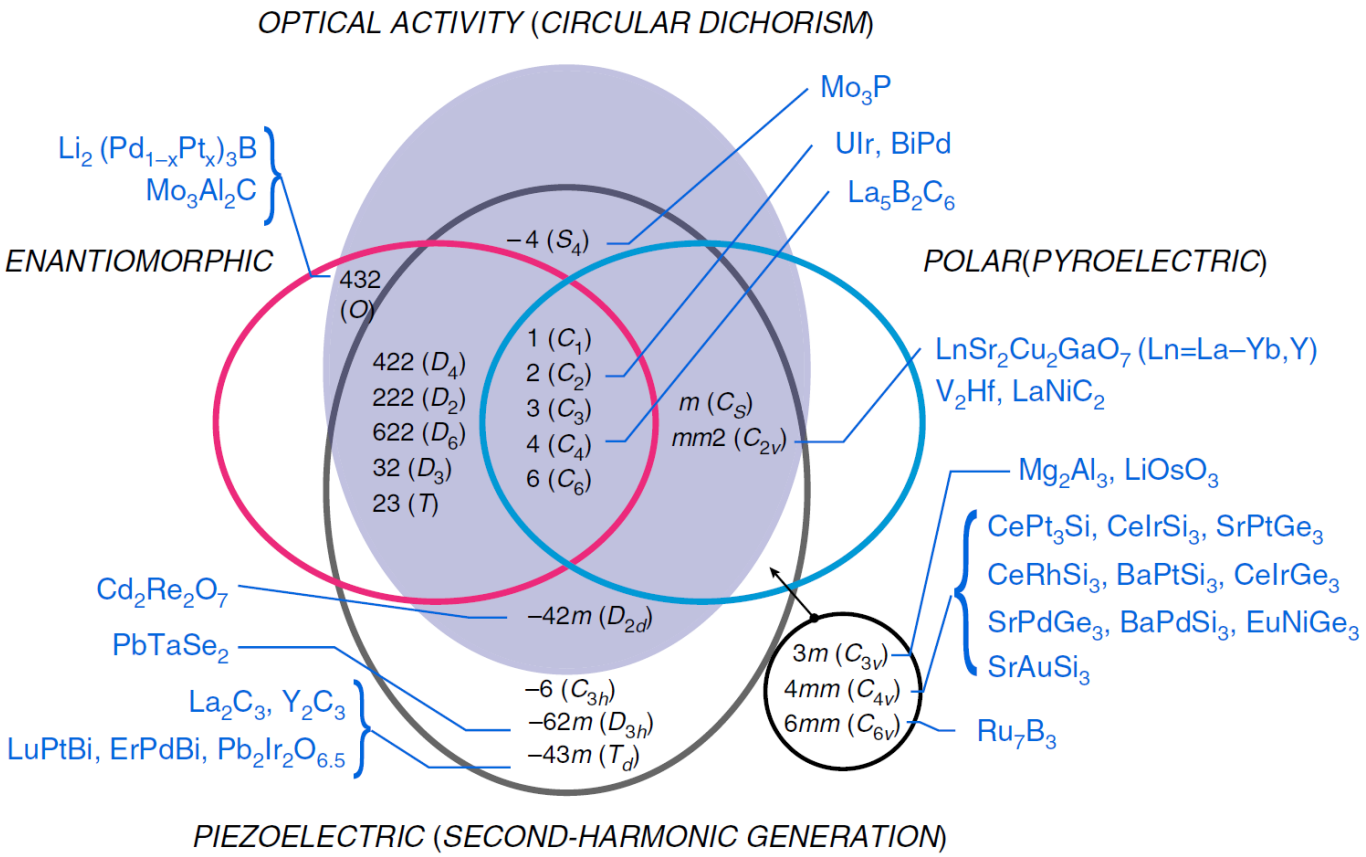




After Halasyamani & Poeppelmeier (1998)

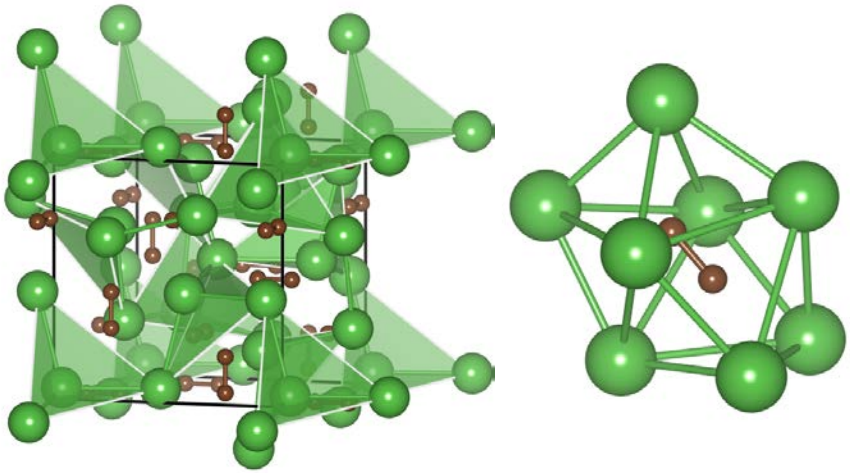
A dearth of NCS metals?

- Most known NCS metals are binary and ternary intermetallics and silicides

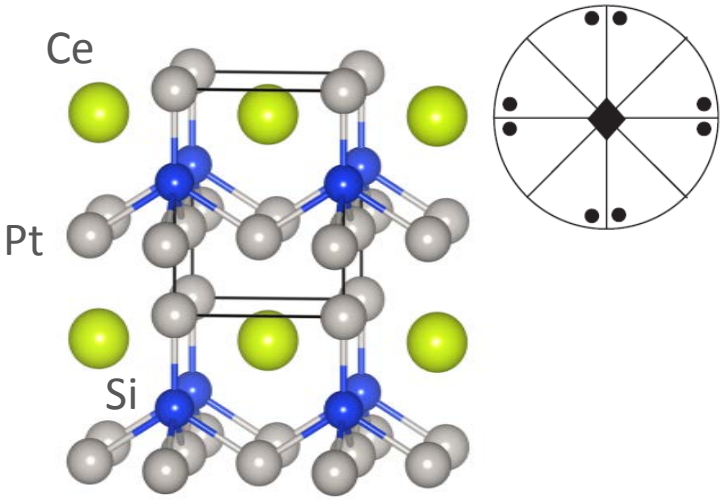


Crystal structures and properties of NCS metals

- La_2C_3
  - bct Pu_2C_3 structure type
  - 14 K superconductor
  - Crystal class: $\bar{4}3m\ (T_d)$



- $CePt_3Si$
  - $CePt_3B$ structure ($AuCu_3$-type)
  - 1 K superconductor
  - Crystal class: $4mm\ (C_{4v})$



$c/a \simeq 1.34$

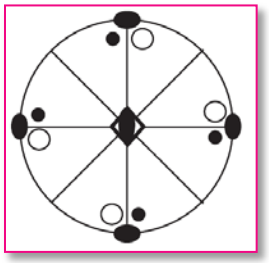
Krupka et al., J. Less-Common Met., **19** 113 (1969)
Kim et al., Phys. Rev. B, **76**, 014516 (2007)

Bauer et al., Phys. Rev. Lett., **92** 027003 (2004)

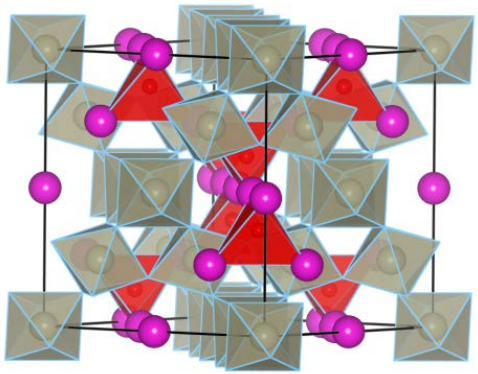
The NCS pyrochlore oxide conductor $Cd_2Re_2O_7$

- Undergoes a complex sequence of phase transitions

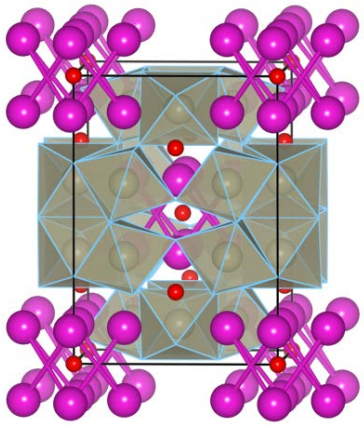
$$Fd\bar{3}m(300\ K) \rightarrow I\bar{4}2m(200\ K) \rightarrow P4_122(< 120\ K)$$



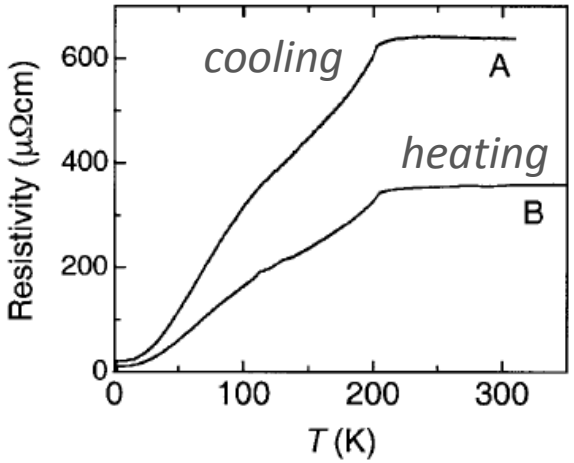
- NCS crystal class: $\bar{4}2m\ (D_{2d})$
- 1 K superconductor, 5d^2 Re electronic configuration



(300 K)



(200 K)



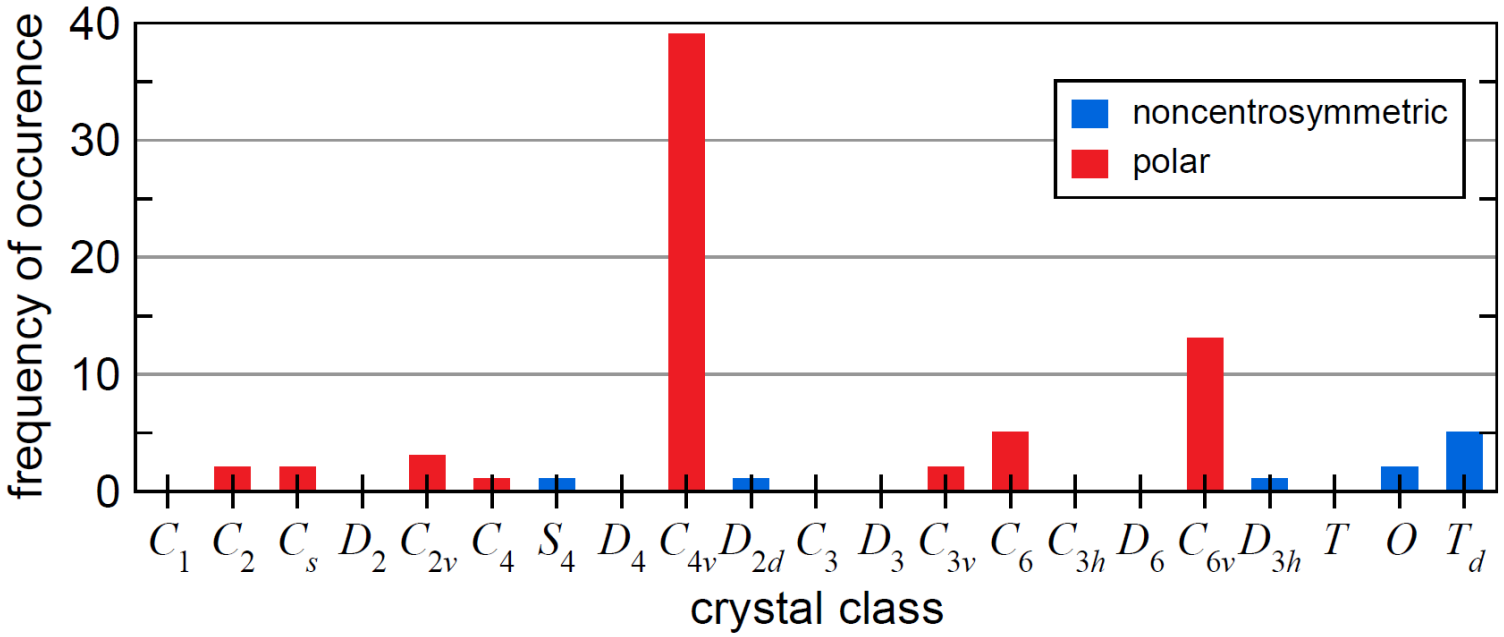
Hanawa et al., Phys. Rev. Lett., **87**, 187001 (2001)

Ohgushi et al., Phys. Rev. B.**83**, 125103 (2011)

A dearth of polar metallic oxides?

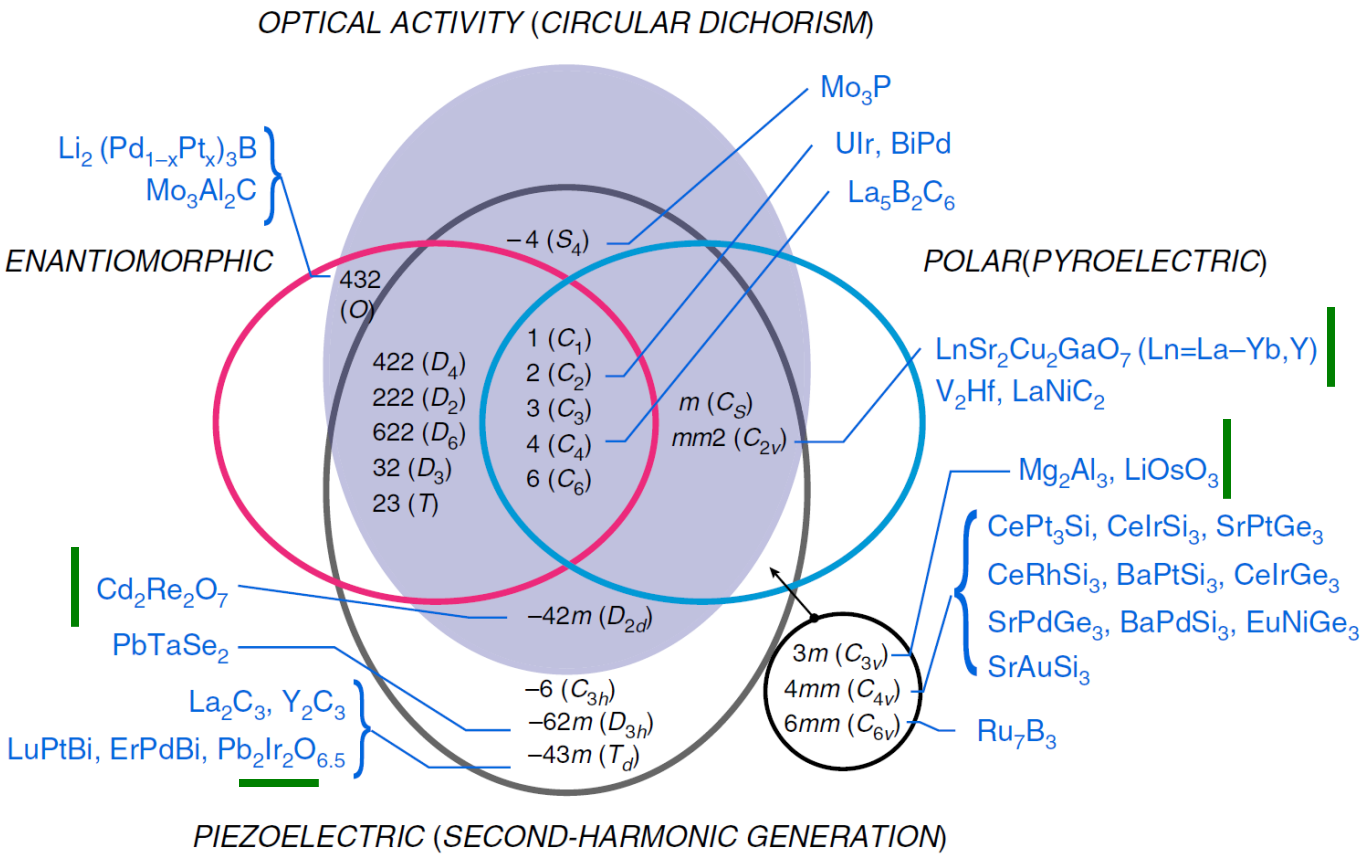
- 78 total compounds (April 29, 2014)
- 67 are polar
- Most are intermetallics (all except ~17),
  - silicides (11), germanates (12), indides (12), …

⇨ Only 2 polar structures are oxides



A dearth of NCS metals?

- Most known NCS metals are binary and ternary intermetallics
- Oxide compounds are particularly elusive (4 known)



A revival in the search of NCS (oxide) metals?

LETTERS
PUBLISHED ONLINE: 22 SEPTEMBER 2013 | DOI: 10.1038/NMAT3754
nature materials

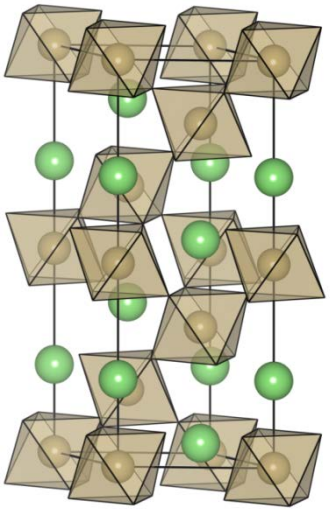
A ferroelectric-like structural transition in a metal

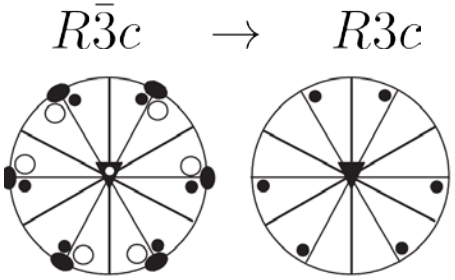
Youguo Shi[1,2†], Yanfeng Guo[1,3†], Xia Wang[1], Andrew J. Princep[3], Dmitry Khalyavin[4], Pascal Manuel[4], Yuichi Michiue[5], Akira Sato[6], Kenji Tsuda[7], Shan Yu[1], Masao Arai[8], Yuichi Shirako[9], Masaki Akaogi[9], Nanlin Wang[2], Kazunari Yamaura[1*] and Andrew T. Boothroyd[3*]

Nat. Mater., **12** 1024 (2013)

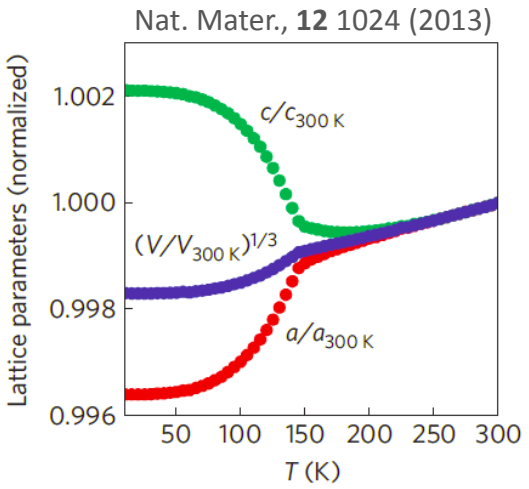
Inversion symmetry breaking in $LiOsO_3$

- Structural transition at near 140 K, $3m\ (C_{3v})$

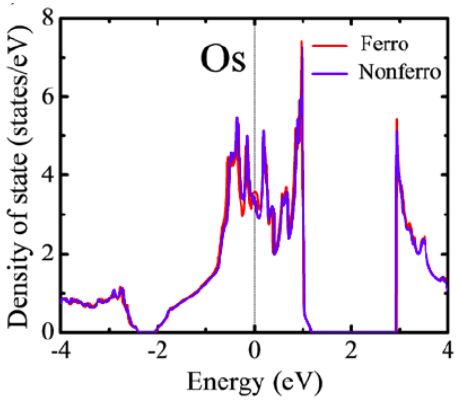




$LiNbO_3$-structure
(low tolerance factor perovskites*)



- Electronic structure at the Fermi level is predominately derived from Os^{5+}



*Benedek & Fennie, J. Phys. Chem. C, **117**, 13339 (2013)
Kim et al., ArXiv: 1311.4139 (2013)

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Nat. Mater., **12** 1024 (2013)

STRUCTURAL TRANSITIONS

'Ferroelectricity' in a metal

The discovery of a ferroelectric-like structural transition in metallic $LiOsO_3$ identifies a new class of materials with unconventional properties, providing an exotic playground for theorists and experimentalists.

Veerle Keppens

Nat. Mater., **12** 952 (2013)

Contraindicated features yield an unusual (useful?) set of properties

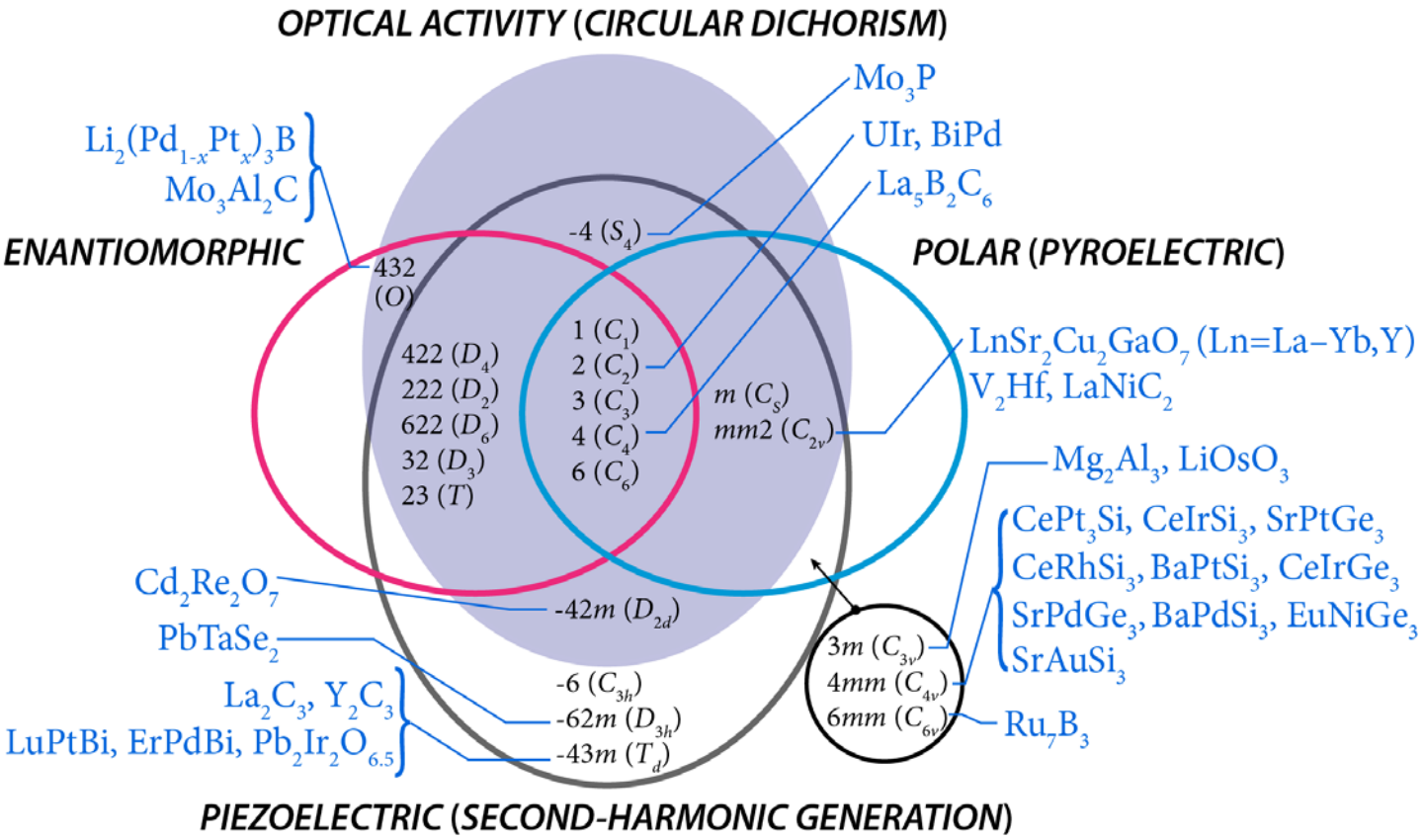
- Optical activity - Kerr rotations
  - Mineev & Yoshioka, Phys. Rev. B, **81**, 094525 (2010)
  - Edelstein, Phys. Rev. B., **83**, 113109 (2011)
- Magnetoelectric effects in superconductors
  - Edelstein, Phys. Rev. Lett., **75**, 2001 (1995)
- Rashba spin-orbit splitting (removal of spin band degeneracies)
  - Ali, Phys. Rev. B, **89** 020505R (2014)
- Unconventional superconductivity (mixed Cooper pairs singlet/triplet)
  - Frigeri, Phys. Rev. Lett., **92** 097001 (2004)

Potential applications remain largely unknown because available materials for characterization and device integration have been limited

Materials Discovery Challenge – Searching for a needle in a haystack

Just because one discovers an example of an noncentrosymmetric metallic oxide, it doesn't mean we know how to create or efficiently find more…

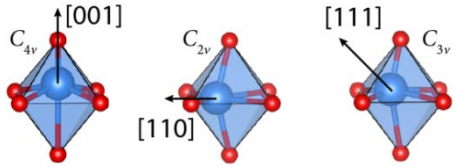
Objective: Discover (by design?) more NCS metallic oxides



Outline

Why are there any NCS metals?

An explanation for inversion symmetry lifting distortions in metals through a weak electron–lattice coupling principle and mode distortion-based classification scheme



NCS metallic oxides by design

First-principles design of a polar ruthenate $(Sr,Ca)Ru_2O_6$ which satisfies

(1) Electronic criterion: itinerant electrons
(2) Structural criterion: noncentrosymmetric crystal

Nature Communications **5**, 3432 (2014)

Physical Properties

- Anisotropic physical properties of a polar metal
- Effect of polar distortions on effective masses
- Effect of polar displacements on electrical conductivity and thermopower

Incompatibility between local polar displacements and metallicity

- Inversion symmetry breaking displacements usually described within vibronic coupling theory* and the second-order Jahn-Teller effect:

* Bersuker, Chem. Rev., **113**, 1351 (2013)

Incompatibility between local polar displacements and metallicity

- Inversion symmetry breaking displacements usually described within vibronic coupling theory* and the second-order Jahn-Teller effect:

$$E = E^{(0)} + \langle 0| \mathcal{H}^{(1)} |0\rangle Q + \frac{1}{2}[\langle 0| \mathcal{H}^{(2)} |0\rangle - 2\sum_{n} \frac{|\langle 0| \mathcal{H}^{(1)} |n\rangle|^2}{E^{(n)} - E^{(0)}}]Q^2 + \ldots$$

first-order JT does not give rise to FE distortions, *non-zero if orbitally degenerate*

second-order JT is a competition between two terms

* Bersuker, Chem. Rev., **113**, 1351 (2013)

Incompatibility between local polar displacements and metallicity

- Inversion symmetry breaking displacements usually described within vibronic coupling theory* and the second-order Jahn-Teller effect:

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second-order JT is a competition between two terms

- A symmetry allowed distortion permits the HOMO and LUMO states to interact, which leads to distortion-dependent hybridization and chemical bond formation

* Bersuker, Chem. Rev., **113**, 1351 (2013)

Incompatibility between local polar displacements and metallicity

- Inversion symmetry breaking displacements usually described within vibronic coupling theory and the second-order Jahn-Teller effect

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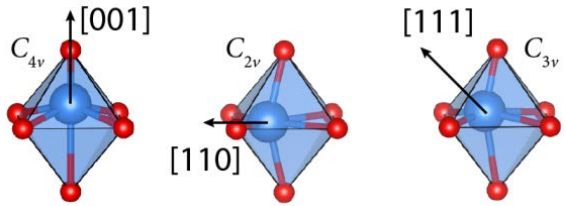
second-order JT

energy lowering term describes the relaxation of the electronic system to atomic displacements (bond formation)

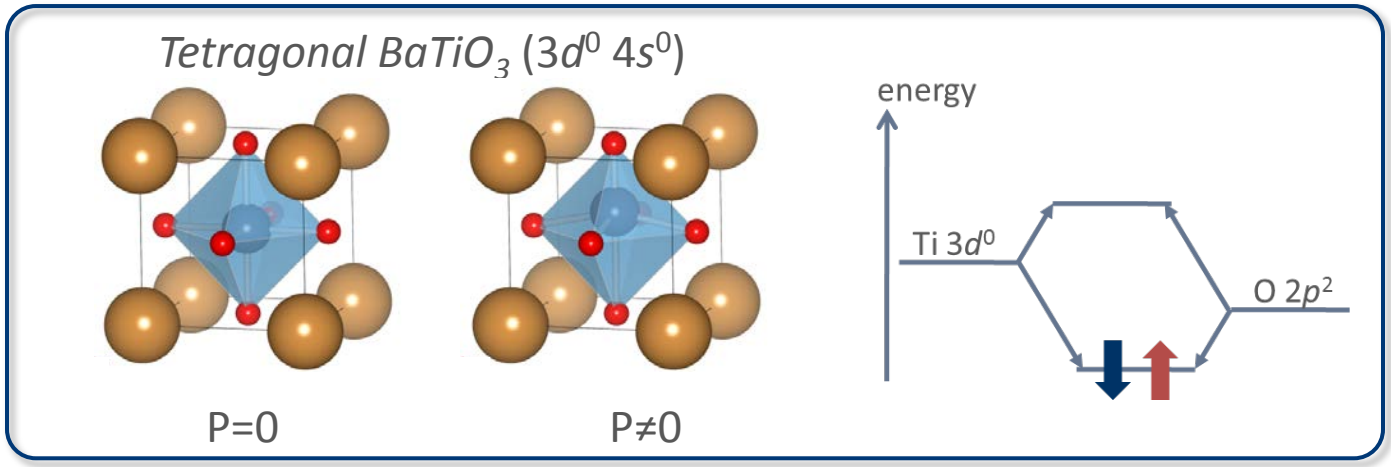
energy raising term describes the short-range repulsive forces and tends to be small in the case of d^0 cations

polar displacements



Itinerant electrons reduce the ligand field stabilization and screen the dipolar interactions favoring cooperative alignment

- Ligand field stabilization of empty cation *d*-orbitals by oxygen *p*-electrons is reduced as electrons are doped into the LUMO

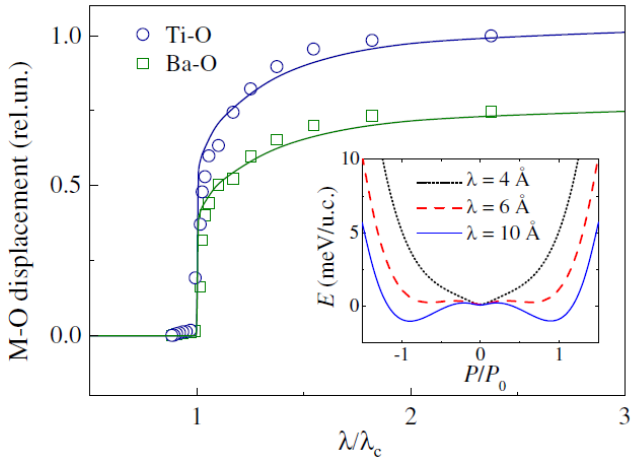


- Screening depends on the number of states at the Fermi level

Thomas-Fermi Screening: $\lambda = \sqrt{\epsilon / e^2 D(E_F)}$

As λ decreases with increase doping, the polar instability diminishes (wells flatten and the displacements vanish, i.e. into the non-polar state)

electron-doped $BaTiO_3$



Wang et al., Phys. Rev. Lett., **109**, 247601 (2012)

Problem!

- How do we rationalize the existence of any NCS metals as a means to formulate design rules for their discovery?

Developing design guidelines for NCS metals

- *Anderson*:

> while free electrons screen out the E field completely, they do not interact very strongly with the transverse optical phonons

- Weak electron–lattice coupling principle (*w-ELCP*):

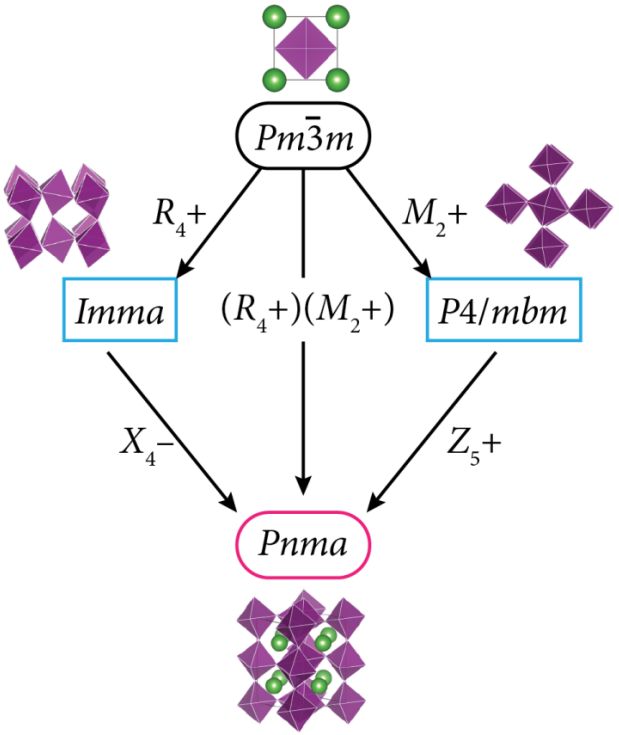
> *NCS metals may exist where there is weak coupling between the electrons at the Fermi level and the (soft) phonon modes responsible for removing inversion symmetry*

Anderson & Blount, Phys. Rev. Lett., **14**, 217 (1965)

Displacive symmetry breaking to find routes to satisfy the *w-ELCP*

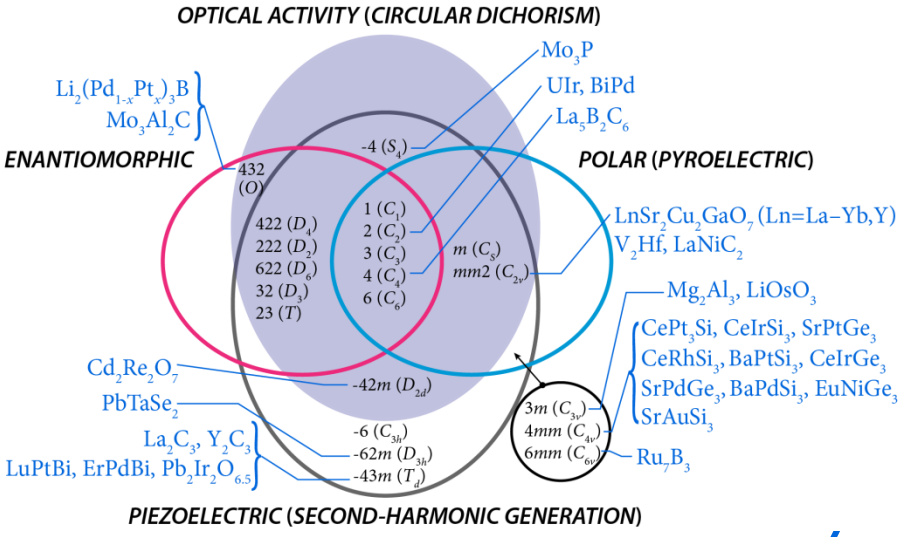
- NCS structure = high-symmetry CS structure + "frozen" distortion modes
  - Apply mode-distortion analysis to characterize atomic displacements or compositional order of a NCS structure relative to a CS structure

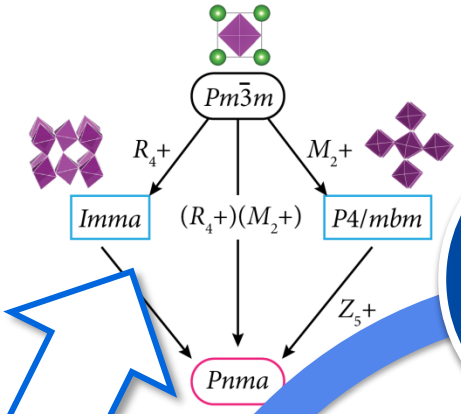
- When a CS structure is unavailable, packing of (acentric) polyhedra is invoked

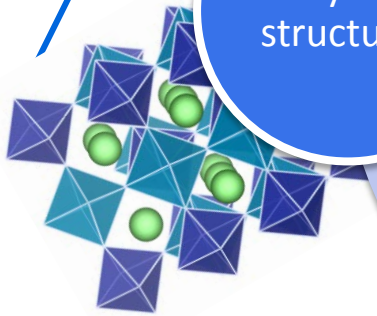


Formulation of a classification scheme

- Use applied group to perform a symmetry-based search on structures of known NCS metals







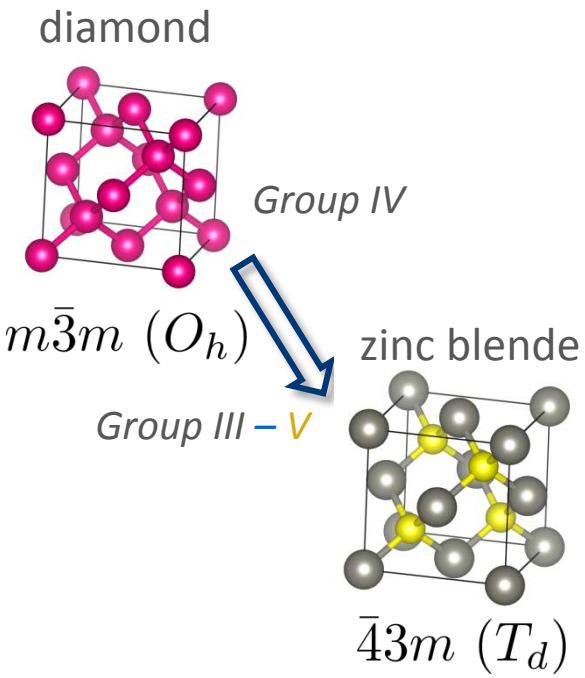
Classification of inversion symmetry lifting routes in metals

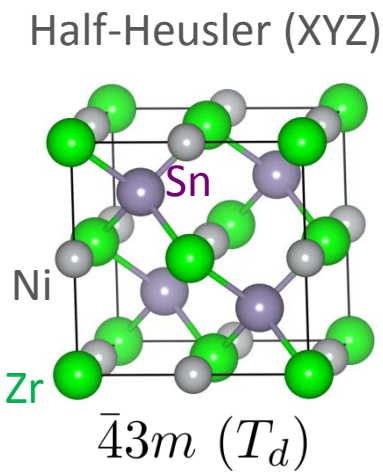
- Symmetry requirements of the lattice (ordering) mode instabilities of a CS reference phase that would drive a NCS transition

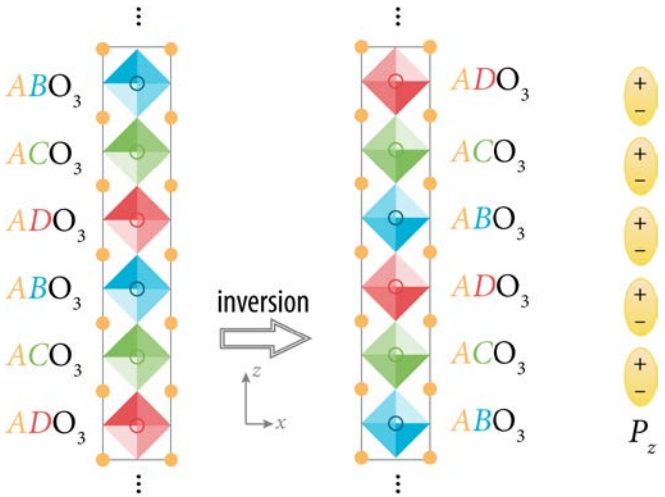
Classification of inversion symmetry lifting routes in metals

- Symmetry requirements of the lattice (ordering) mode instabilities of a CS reference phase that would drive a NCS transition

Inversion Lifting Method		Mode Requirements	Description
(1)	Compositional Order	None	Decorating one or more interleaved lattices with multiple cations







tri-color perovskites superlattices

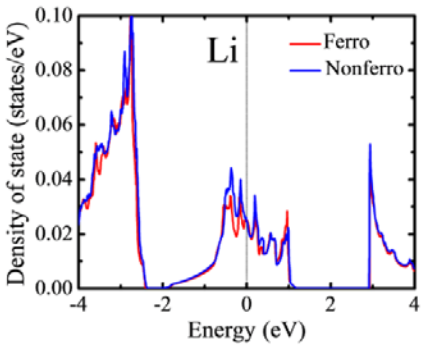
Classification of inversion symmetry lifting routes in metals

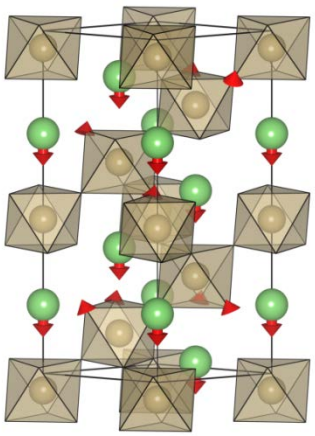
- Symmetry requirements of the lattice (ordering) mode instabilities of a CS reference phase that would drive a NCS transition

Inversion Lifting Method	Mode Requirements	Description
(2) Packing of Acentric Polyhedra	1, *k*=0 *or* *k*≠0 mode	Alignment of acentric polyhedra obtained from cations that undergo "out-of-center" displacements and contribute few states near the Fermi level or intrinsically NCS units

$LiOsO_3$: single irrep (Γ_2^-)

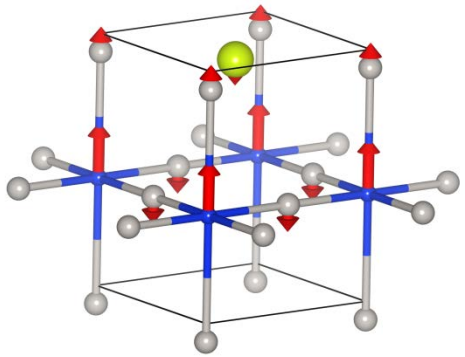
ATOM	DISPLACEMENT (Å)	NORM. AMP.
Li	0.394	0.88
Os	0.073	0.16
O	0.116	0.45





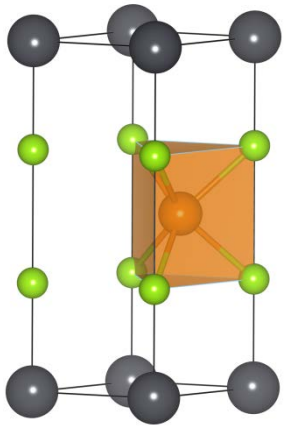
Kim et al., ArXiv: 1311.4139
Xiang, ArXiv: 1312.4225

$CePt_3Si$: single irrep (Γ_3^-)



Bauer et al., Phys. Rev. Lett., **92** 027003 (2004)

$PbTaSe_2$



packing of trigonal prisms

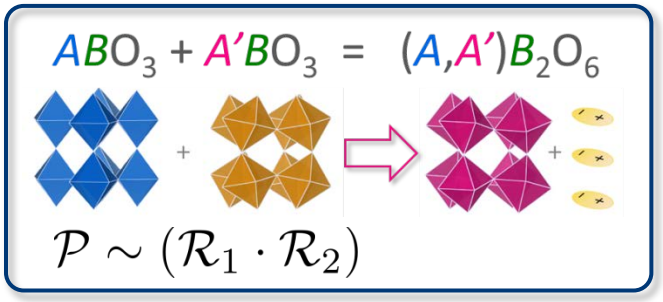
Ali, Phys. Rev. B, **89** 020505R (2014)

Classification of inversion symmetry lifting routes in metals

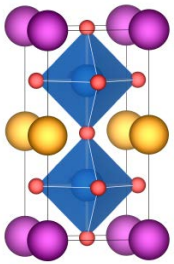
- Symmetry requirements of the lattice (ordering) mode instabilities of a CS reference phase that would drive a NCS transition

Inversion Lifting Method	Mode Requirements	Description
(3) Geometric-induced Displacements	≥2, $k \neq 0$ coupled modes	Anharmonic coupling of centric lattice modes involving both cations and anions that do not lead to Fermi surface gapping

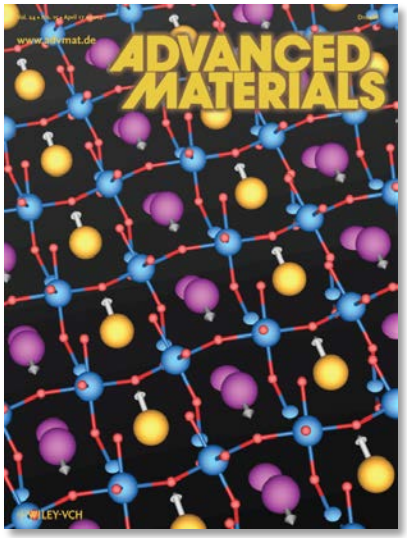
Analogous set of guidelines for (hybrid*) improper ferroelectricity in perovskite superlattices



Rotations induce a polarization through **trilinear linear coupling** interaction in the free energy



No SOJT cations are needed to lift inversion



JMR & Fennie, Adv. Mater., **24** 1961 (2012)

*Benedek & Fennie, PRL, **106** 107204 (2011)

Classification of inversion symmetry lifting routes in metals

- Symmetry requirements of the lattice (ordering) mode instabilities of a CS reference phase that would drive a NCS transition

Inversion Lifting Method		Mode Requirements	Description
(1)	Compositional Order	None	Decorating one or more interleaved lattices with multiple cations
(2)	Packing of Acentric Polyhedra	1, k=0 *or* $k\neq0$ mode	Alignment of acentric polyhedra obtained from cations that undergo "out-of-center" displacements and contribute few states near the Fermi level or Aintrinsically NCS units
(3)	Geometric-induced Displacements	≥2, $k\neq0$ coupled modes	Anharmonic coupling of centric lattice modes involving both cations and anions that do not lead to Fermi surface gapping

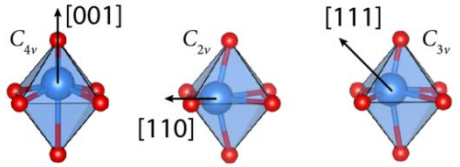
Exploit mechanism (3) to design a NCS metal

➡ Effectively decouple the atomic structure from the electronic states at the Fermi level – fulfilling the weak coupling *principle*

Outline

Why are there any NCS metals?

An explanation for inversion symmetry lifting distortions in metals through a weak electron–lattice coupling principle and mode distortion-based classification scheme



NCS metallic oxides by design

First-principles design of a polar ruthenate $(Sr,Ca)Ru_2O_6$ which satisfies

(1) Electronic criterion: itinerant electrons
(2) Structural criterion: noncentrosymmetric crystal structure

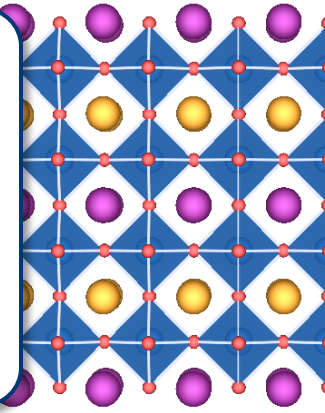
Nature Communications **5**, 3432 (2014)

Physical Properties

- Anisotropic physical properties of a polar metal
- Effect of polar distortions on effective masses
- Effect of polar displacements on electrical conductivity and thermopower

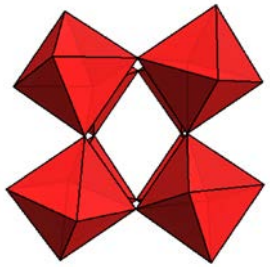
Design of a NCS oxide metal based on the weak-coupling *w-ELCP*

$(A',A)B_2O_6$



Structural Criterion

Anharmonic coupling of two zone boundary instabilities to lift inversion symmetry (route 3)



⇨ A/A' (001) layered perovskites with orthorhombic tilts

Selection Criterion

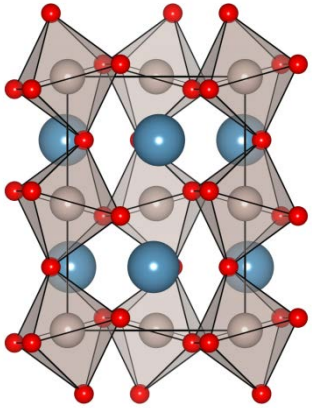
Transition metal cations with partially filled *d*-electron states and broad bands

⇨ 4*d* transition metals

V	Cr	Mn	Fe	Co	Ni	Cu
41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag

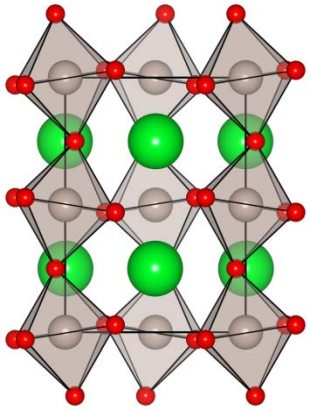
Selection criterion – divalent perovskite ruthenates $A^{2+}RuO_3$

- $CaRuO_3$ (CRO)



$a^-a^-c^+$ tilt pattern
rotation angle: 10.2°
tilt angle: 15.2°
Ru–O–Ru ∠: 150°

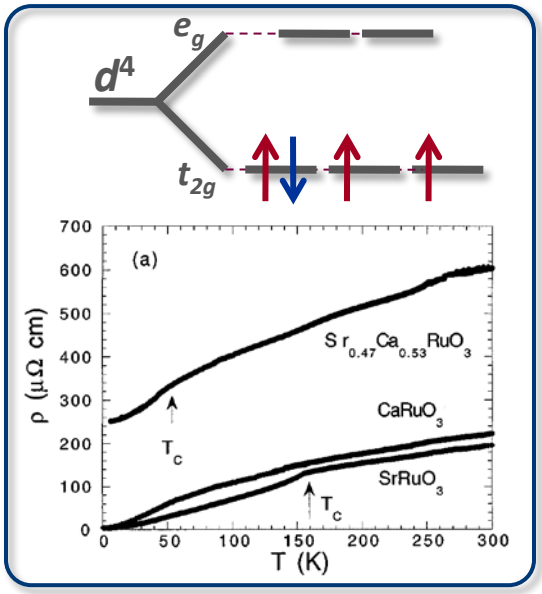
- $SrRuO_3$ (SRO)



$a^-a^-c^+$ tilt pattern
rotation angle: 6.2°
tilt angle: 8.7°
Ru–O–Ru ∠: 161°

- Weakly correlated metals
  - Low spin Ru^{4+}: t_{2g}^4 electronic configuration
  - CRO is a paramagnetic metal
  - SRO is a ferromagnetic metal (150 K)

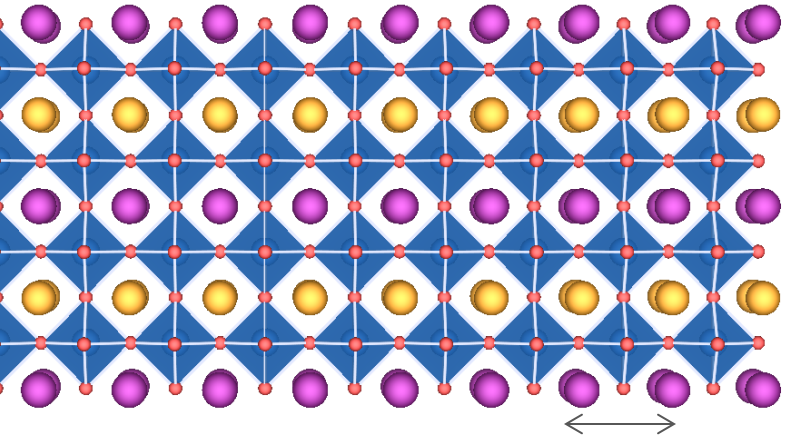
- $Sr_{1-x}Ca_xRuO_3$ solid solutions (x=0.5) are conducting and ferromagnetic



G. Cao et al., Phys. Rev. B, **56** 321 (1997); Keawprak et al., J. Alloy Comp., **523** 182 (2012)

First-principles validation of materials design criteria

- Compute ground state structures and identify primary modes (atomic displacements) that lead to the ground state structure
  - VASP LSDA calculations with variable cell/volume/atomic relaxation
  - PAW pseudopotentials
  - 550 eV planewave energy cutoff
  - Constrained $a = b$ to mimic epitaxial growth of material on a substrate with a square surface net



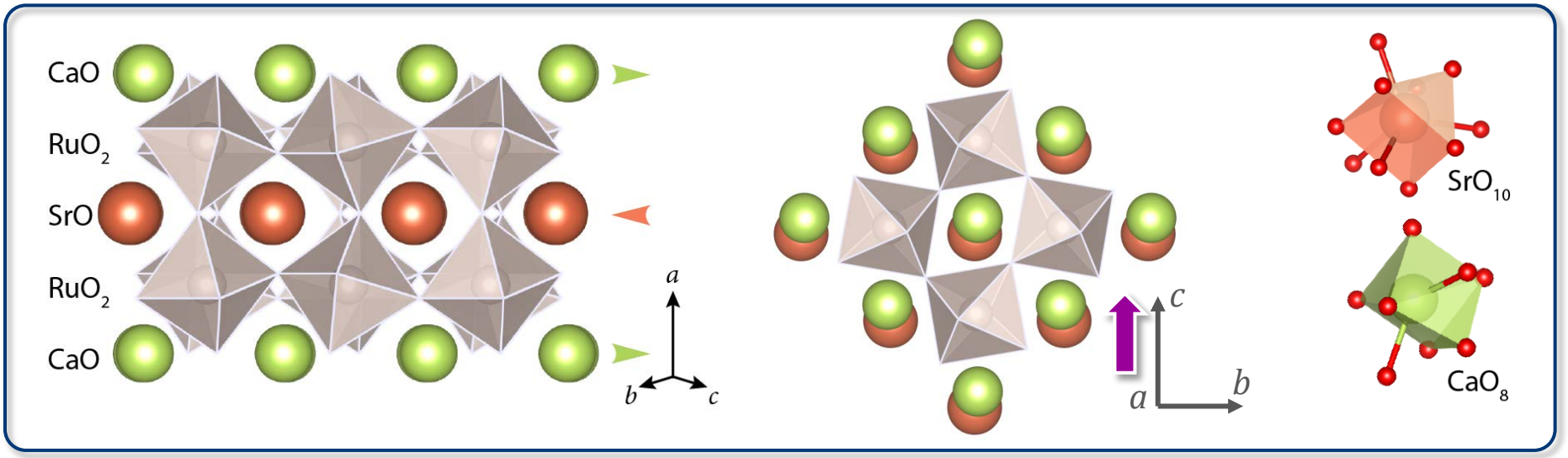
$(Sr,Ca)Ru_2O_6$

Examined 30+ unique symmetries with the (001) ordered Sr and Ca sublattice

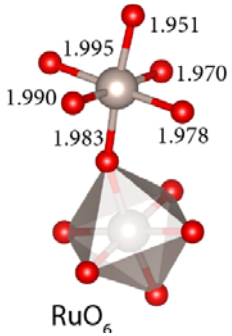
P.E. Blöchl, Phys. Rev. B **50** 17953 (1994); G. Kresse and J. Furthmuller, Phys. Rev. B **54** 11169 (1996)
G. Kresse and D. Joubert, Phys. Rev. B **59** 1758 (1999)

Ground state structure is polar with the targeted orthorhombic octahedral rotations and inversion lifting cation displacements

- Exhibits the $a^-a^-c^+$ tilt pattern tilt pattern in space group $Pmc2_1$ (C_{2v})
  - 157.1° and 145.6° Ru–O–Ru bond angles along the ordering direction
  - 150.4° Ru–O–Ru bond angles within the layers

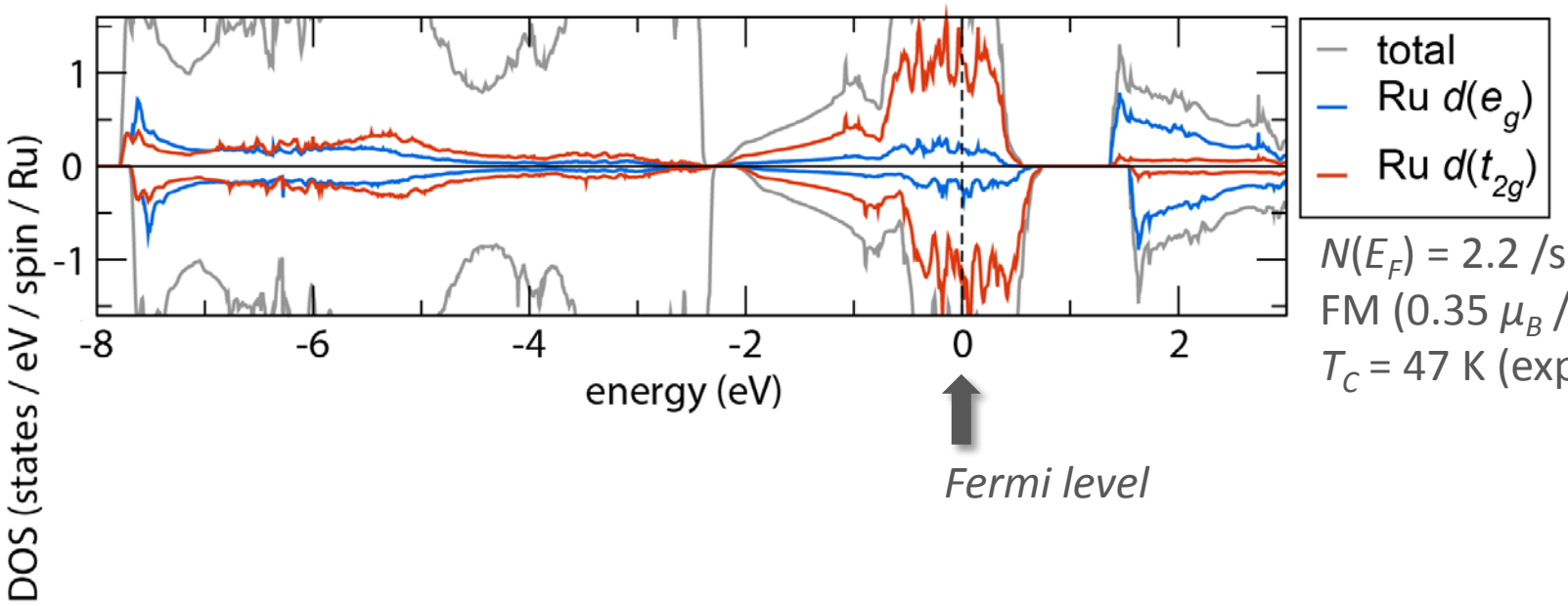


- Out-of-center Ru^{4+} displacements



Electronic structure of cation ordered $(Sr,Ca)Ru_2O_6$

- Valence band is composed of strongly hybridized O 2*p* and Ru 4*d* states
  - Sharp peaks near the Fermi level are from the weak dispersion in the t_{2g} bands
  - Broad e_g bands form the conduction band (near 1.5 eV)



$N(E_F)$ = 2.2 /spin/Ru
FM (0.35 μ_B / Ru)
T_C = 47 K (exp = 57 K)

Electronic structure of cation ordered (Sr,Ca)Ru_2O_6

- Valence band is composed of strongly hybridized O 2*p* and Ru 4*d* states
  - Sharp peaks near the Fermi level are from the weak dispersion in the t_{2g} bands
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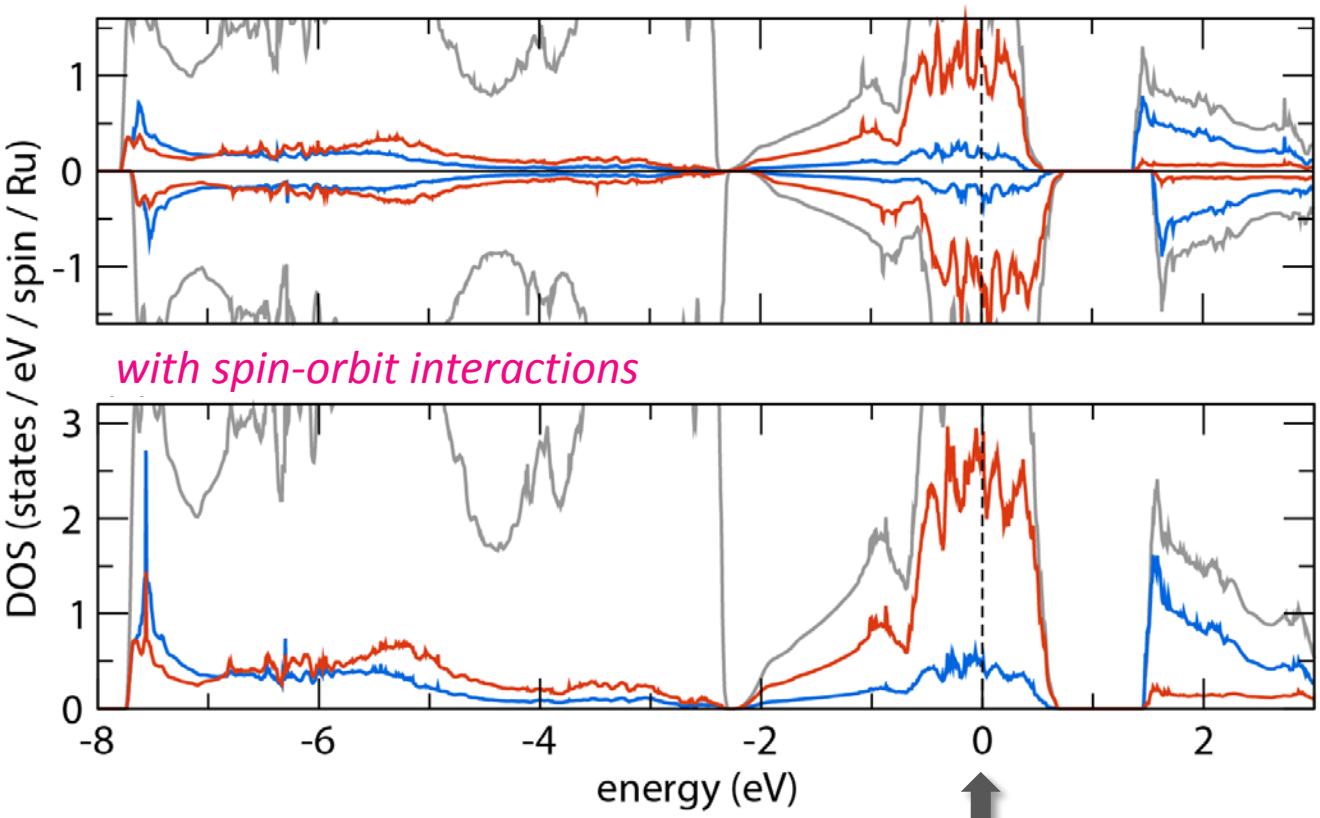


$N(E_F)$ = 2.2/spin/Ru
FM (0.35 μ_B/Ru)
T_C = 47 K

$N(E_F)$ = 4.36/Ru
FM (~0.06 μ_B/Ru)

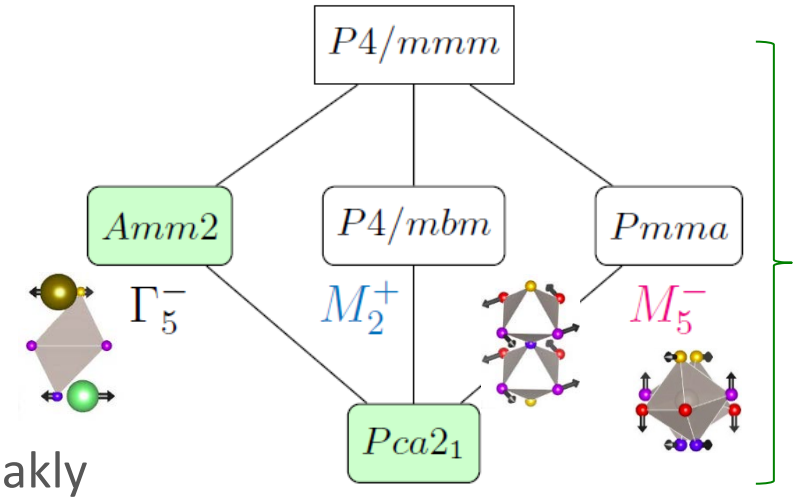
⇨ Robust conductor

Fermi level

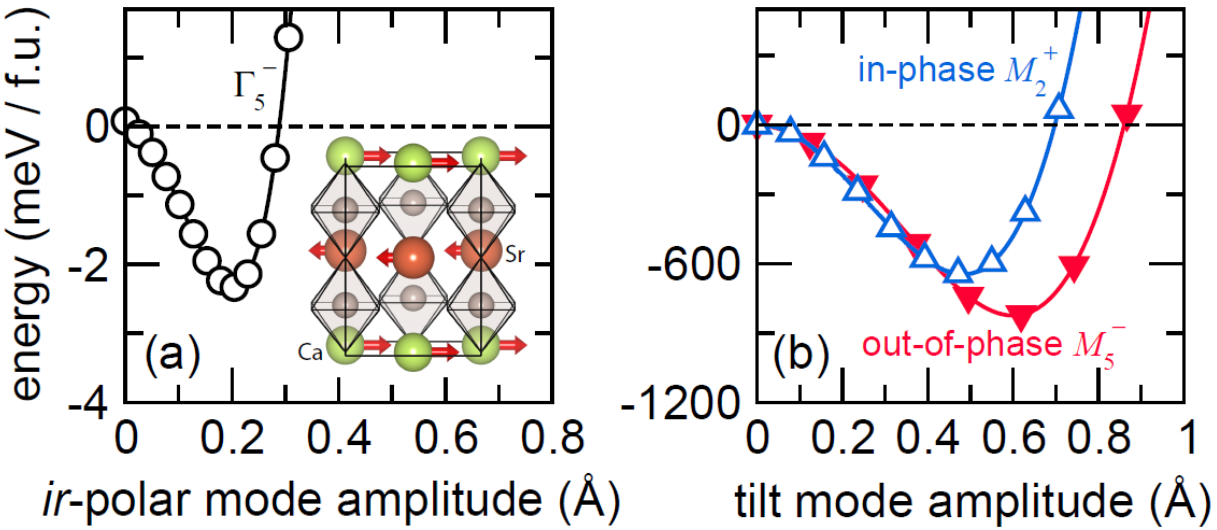
Stability of the polar *Pca*2_1 ground state structure

- Three modes dominate the equilibrium structure

$$\xi \simeq 0.32\Gamma_5^- + 0.54M_2^+ + 0.78M_5^-$$

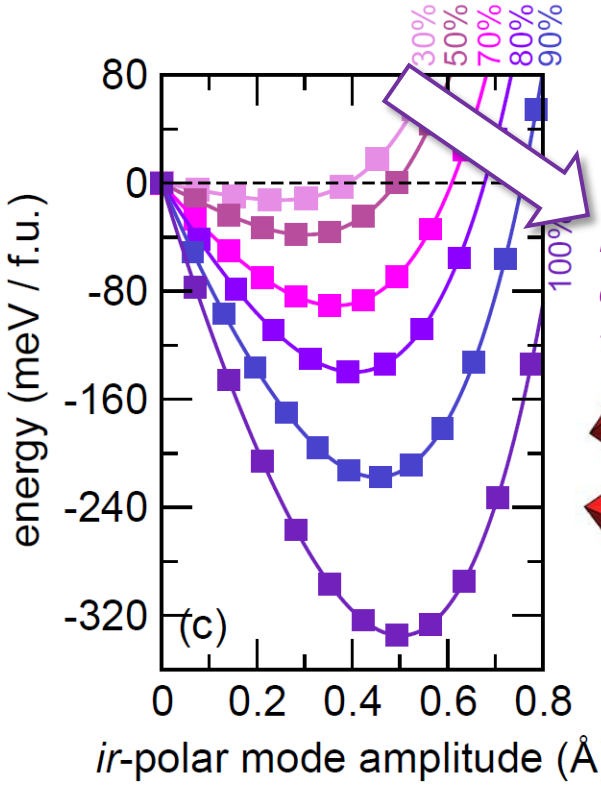


- The polar atomic displacements are weakly unstable in the CS structure
- The *k*≠0 rotational modes dominate the energetic stability of (Sr,Ca)Ru_2O_6

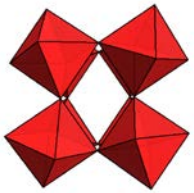


Anharmonic interaction between rotations and polar mode provide structure stability (route 3)

- Non-polar modes cooperatively interact to stabilize the polar the structure
  - Induced polar Sr and Ca atomic displacements lift inversion symmetry



Increasing amplitude of orthorhombic tilt pattern



$\mathcal{F} \sim q \cdot (\mathcal{Q}_1 \cdot \mathcal{Q}_2)$

polar displacements

M_5^- *out-of-phase rotations*

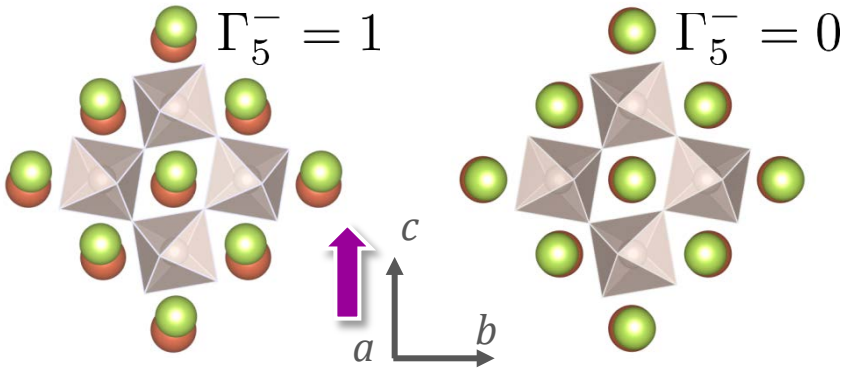
M_2^+ *in-phase octahedral rotations*

These two modes alone lift inversion symmetry

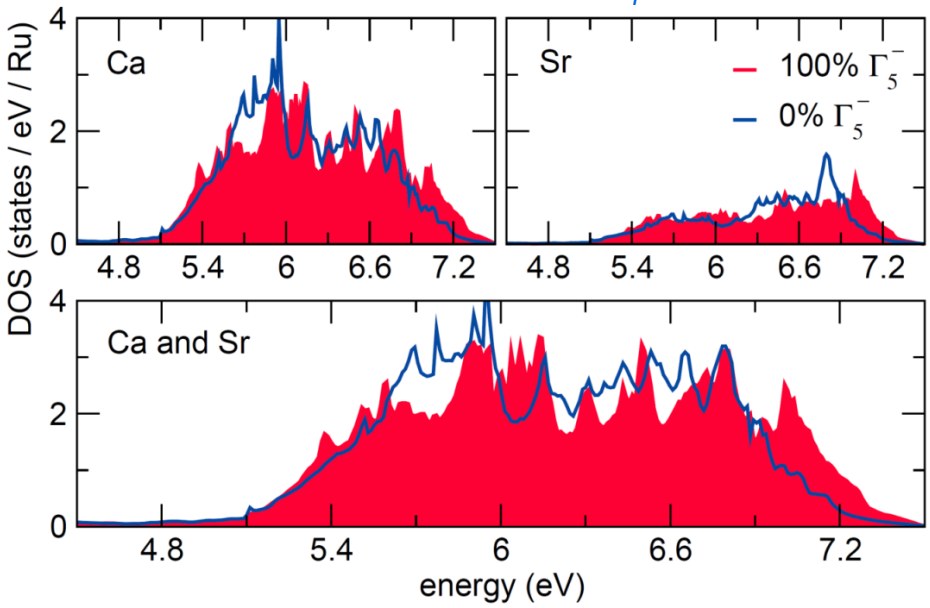
weak, secondary mode, triggered by anharmonic coupling to primary modes

Fulfilling the weak coupling principle

- Induced polar displacements shift the Ca and Sr atoms along the *c*-axis

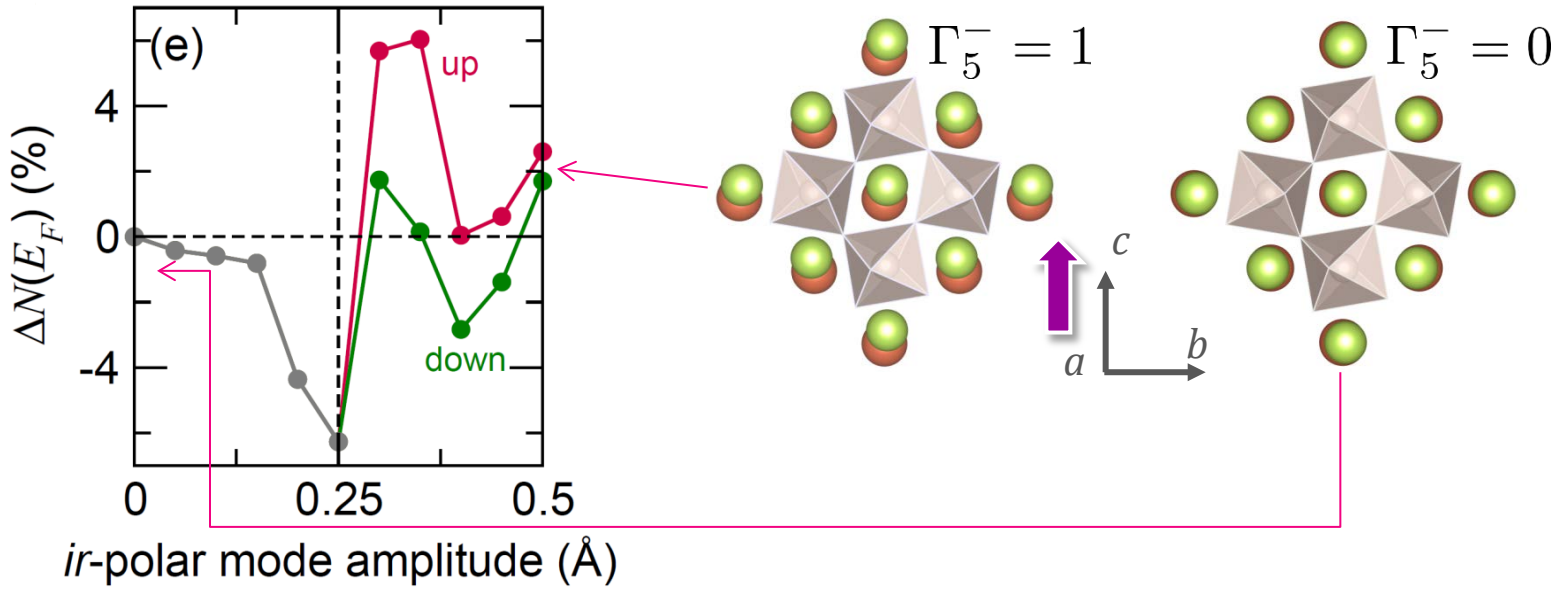


These atoms contribute states to the electronic structure far from E_F



Spin–phonon coupling in $(Sr,Ca)Ru_2O_6$

- Induced polar displacements of the Ca and Sr atoms change the stability of the magnetic ground state
- Change in number of states at the Fermi-level relative to the rotational distorted structure without an polar displacements (Γ_5^-)

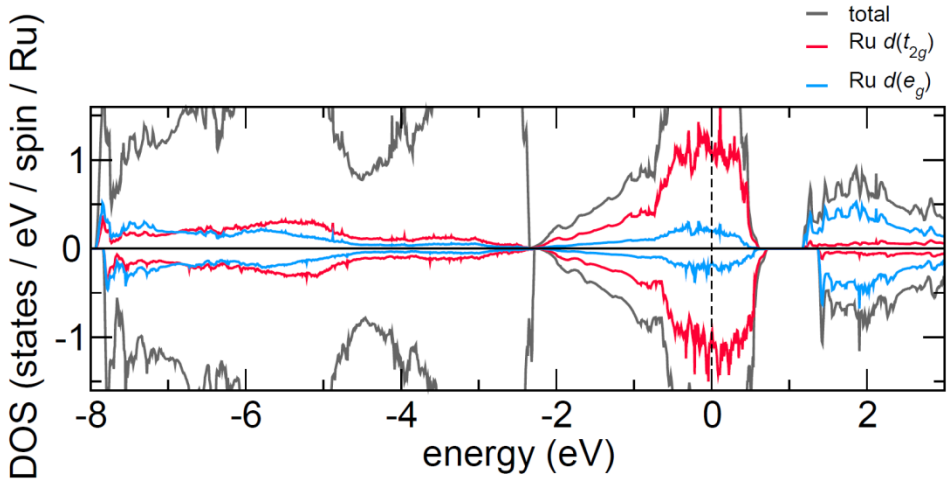


➡ polar mode (A-site displacements) is also critical to stabilizing FM state

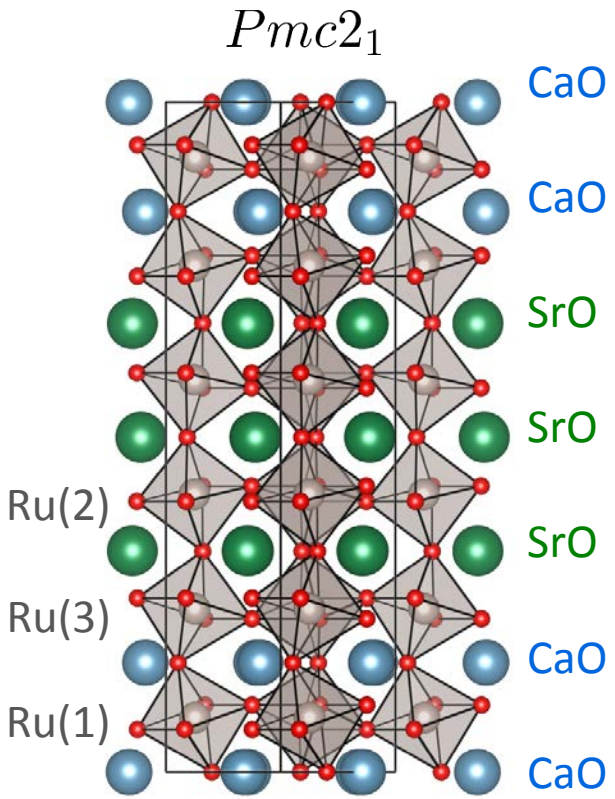
Where to look for more polar metallic oxides?

$(SrRuO_3)_3/(CaRuO_3)_3$ superlattice on (001) $NdGaO_3$

- DOS consistent with low-spin Ru^{4+} and the metallicity is maintained



Ru atom	Moment (μ_B)
Ru(1)	+0.15
Ru(2)	+0.40
Ru(3)	-0.02



➡ Ru(3) local moments at the interface are reduced and anti-aligned to those of Ru(1) and Ru(2)

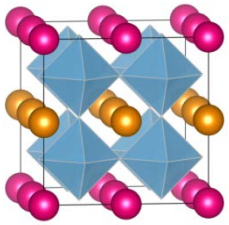
*In collaboration with CB Eom (Wisconsin)

Control over anharmonic interactions with artificial cation order

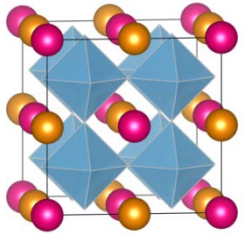
- *Where to look for more polar metallic oxides*?
  - Generalization of the approach to new artificial oxides
  - Judicious selection of d^n cations: vanadates, molybdates, etc.

Extended to "simple" ordering schemes and all possible rotations for $(A,A')(B,B')O_6$

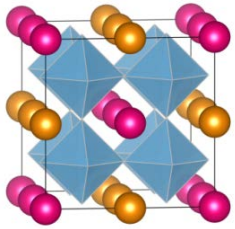
[001] ordered "Layered"



[110] ordered "Columnar"



[111] ordered "Rock Salt"



CHEMISTRY OF MATERIALS

Article

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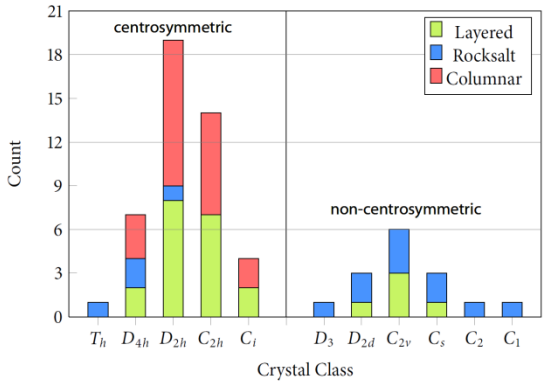
Atomic Scale Design of Polar Perovskite Oxides without Second-Order Jahn–Teller Ions

Joshua Young and James M. Rondinelli*

Chem. Mater., **25** 4545 (2013)



Geometric-induced displacements using changes in lattice geometry

- *Where to look for more polar metallic oxides*?
  - Generalization of the approach to layered low-dimensional oxides

Ruddlesden-Popper *n*=1 structures with or without cation ordering (anharmonic coupling alone)

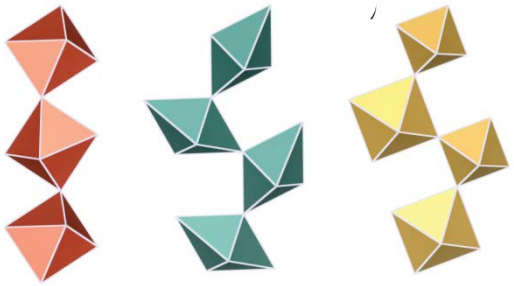
Inorganic Chemistry
Inorg. Chem., **53** 336 (2014) Article
pubs.acs.org/IC

Crystal-Chemistry Guidelines for Noncentrosymmetric A_2BO_4 Ruddlesden–Popper Oxides

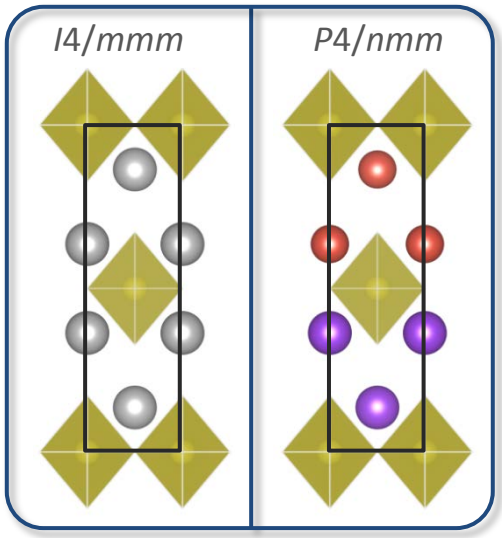
Prasanna V. Balachandran, Danilo Puggioni, and James M. Rondinelli*

Anharmonic interactions

$$\mathcal{F} \sim P \cdot Q_1^n \cdot Q_2^m$$



RP superlattices



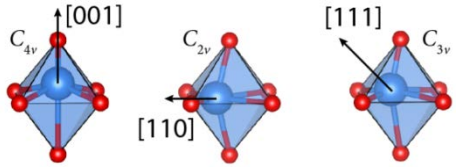
$(A,A')B_2O_4$

Drexel UNIVERSITY

Outline

Why are there any NCS metals?

An explanation for inversion symmetry lifting distortions in metals through a weak electron–lattice coupling principle and mode distortion-based classification scheme



NCS metallic oxides by design

First-principles design of a polar ruthenate $(Sr,Ca)Ru_2O_6$ which satisfies

(1) Electronic criterion: itinerant electrons
(2) Structural criterion: noncentrosymmetric crystal structure

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Physical Properties

- Anisotropic physical properties of a polar metal
- Effect of polar distortions on effective masses
- Effect of polar displacements on electrical conductivity and thermopower